

The University of Chicago

A STUDY OF THE ACTION OF THE
GRIGNARD REAGENT ON
AROMATIC OXIMES

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1932

By

KENNETH NIELSEN CAMPBELL

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

1935

The University of Chicago

A STUDY OF THE ACTION OF THE
GRIGNARD REAGENT ON
AROMATIC OXIMES

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1932

By

KENNETH NIELSEN CAMPBELL

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

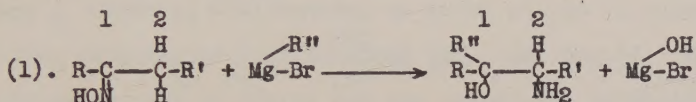
1935



A STUDY OF THE ACTION OF THE GRIGNARD
REAGENT ON AROMATIC OXIMES

I. INTRODUCTION

The action of the Grignard reagent on aldoximes and ketoximes has been studied in a few cases.¹ Stieglitz and his collaborators have been able to prepare several β -amino alcohols² (alkamines) by the action of Grignard reagents³ on ketoximes. This work has resulted in the discovery of what is apparently a new type of rearrangement,⁴ the migration of a nitrogen atom from one carbon atom to another:



¹Busch and Hobein, Ber., **40**, 2096 (1907); Diels and ter Meer, Ber., **42**, 1940 (1909); Angeli, Alessandri and Alazzi-Mancini, C., **1911**, II, 606; C.A., **5**, 3403 (1911).

²M. E. Maver, Doctorate Dissertation, University of Chicago, 1926. Abstracts of Theses, University of Chicago, Science Series, IV (1925-26), 111-16.

W. E. Sturgeon found that 1,1-diphenyl-1-hydroxy-2-amino-propane, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})-\text{CH}(\text{NH}_2)\text{CH}_3$, was formed when propiophenone oxime reacted with phenylmagnesium bromide. Doctorate Dissertation, University of Chicago, 1929. Abstracts of Theses, University of Chicago, Science Series, VIII (1929-30), 145-53.

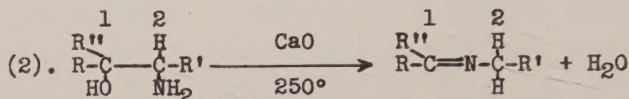
J. E. Cole obtained β,β -diphenyl- β -hydroxyethylamine, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{CH}_2\text{NH}_2$, by the reaction of phenylmagnesium bromide on acetophenone oxime. Doctorate Dissertation, University of Chicago, 1929. Abstracts of Theses, University of Chicago, Science Series, VII (1928-29), 145-50.

³The Grignard reagent used in this work is in a very concentrated form. See the Experimental Part.

⁴Cole, loc. cit.

The nitrogen atom has migrated from carbon atom (1) to carbon atom (2) during the course of the reaction.

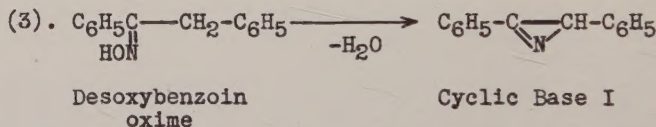
Stieglitz and his students^{1,2} have also shown that these alkamines under the influence of calcium oxide or other bases at elevated temperatures rearrange again, probably to form N-substituted imides:*



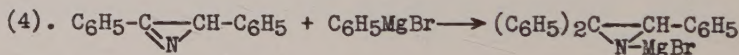
By this reaction the nitrogen atom has again become attached to carbon atom (1), while remaining linked to carbon atom (2).

At present, as a working hypothesis, one might assume the existence of cyclic bases as intermediate products in the reactions (1) and (2). The study of this hypothesis, expressed in the following equations, was the object of this research.

In the case of reaction (1) the following mechanism would then be indicated, desoxybenzoin oxime being used as a typical case:



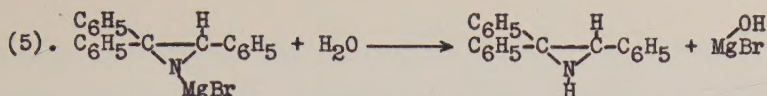
In reaction (3) the dehydration might be due to the concentrated Grignard reagent.



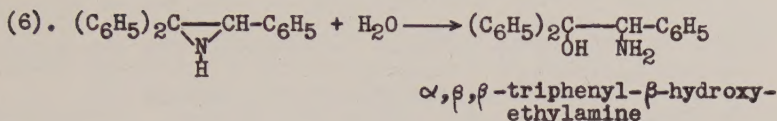
¹ Maver, Cole, Sturgeon, *loc. cit.*

² C. W. Lenth, Doctorate Dissertation, University of Chicago, 1930. Abstracts of Theses, University of Chicago, Science Series, VIII (1929-30), 101-109.

*Note: Recent results of Stieglitz and H. S. Bloch prove that the products of this second action are indeed the ring derivatives (cyclic bases II) postulated by Mr. Campbell as probable intermediate compounds.-- J. Stieglitz, October, 1934.

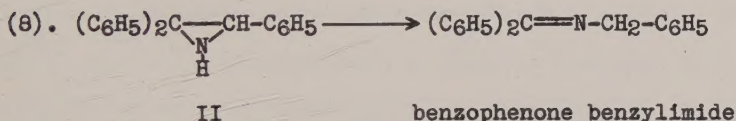
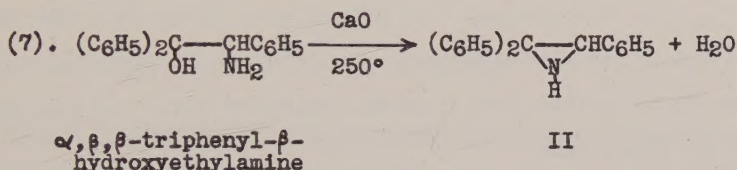


Cyclic Base II



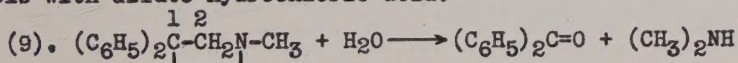
Reactions (5) and (6) probably take place simultaneously or in rapid sequence.

A mechanism for reaction (2) has been partially confirmed by Lenth.¹ When applied to α, β, β -triphenyl- β -hydroxyethylamine it gives the reactions below:



The cyclic base II is assumed to be an intermediate in both reactions (1) and (2). It is very probable that it might rupture differently in reactions (1) and (2) because the condi-

¹Lenth, during his work on N-methyl- β, β -diphenyl- β -hydroxyethylamine, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH}) - \text{CH}_2(\text{NHCH}_3)$, successfully isolated the N-methylated cyclic base, 1,1-diphenyl-N-methyl-ethylenimine, $(\text{C}_6\text{H}_5)_2\text{C} - \text{CH}_2 - \text{N} - \text{CH}_3$. It forms benzophenone and dimethylamine on hydrolysis with dilute hydrochloric acid:



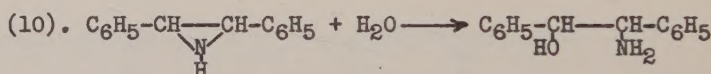
This involves a break of the carbon (1) carbon (2) bond, exactly as it occurs in reaction (2), whose end product, $\text{R}(\text{R}')\text{C} = \text{N} - \text{CH}_2\text{R}'$, on hydrolysis forms a ketone and an amine.

tions are so radically different. In reaction (1) acid and moisture are present, while reaction (2) is carried out under anhydrous conditions at a high temperature. Since reaction (2) was not studied in this investigation, it will not be discussed further. The following evidence is available for the support of the mechanism set forth as explanation of reaction (1).

1. Neber and Burgard¹ have prepared the cyclic base $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{-CH}\text{---}\text{C-CH}_3$. It is, therefore, possible that other cyclic bases of this type² may exist.

2. Lenth³ isolated the compound $(\text{C}_6\text{H}_5)_2\text{-C}\text{---}\text{CH}_2$, 1,1-diphenyl-N-methyl-ethylenimine. There are many other compounds⁴ of type II recorded in the literature.

3. Weiszberger⁵ and others have shown that the compound cis α,β -diphenylethylenimine yields α -amino- β -hydroxydibenzyl when it is heated with 2-normal sulphuric acid for one half hour on the water bath:



An hydrolysis of this type might take place under milder conditions in the presence of a Grignard mixture.

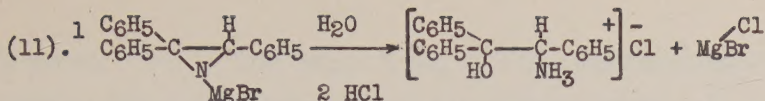
¹Neber and Burgard, Ann., **493**, 281-94 (1932).

²A cyclic base (type I) might easily be changed to the ethylenimine base (type II) by means of the Grignard reagent.

³Lenth, loc. cit.

⁴Darapsky and Spannagel, J. prakt. Chem., **92**, 272-96 (1915). For a review of the literature see Hollins, C., The Synthesis of Nitrogen Rings, (London: Ernest Benn. Limited, 1924), pp. 2-21.

⁵Weiszberger and Bach, Ber., **64**, 1105 (1931).



In order to obtain further information as to the role of triatomic rings of nitrogen and carbon in rearrangement reactions of this type, the study of the formation of α, β, β -triphenyl- β -hydroxyethylamine, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})-\text{CH}(\text{NH}_2)\text{C}_6\text{H}_5$, was undertaken at the suggestion of Professor Stieglitz. It was hoped that it could be prepared directly by the action of phenylmagnesium bromide on desoxybenzoin oxime, $\text{C}_6\text{H}_5-\text{C}(=\text{NOH})-\text{CH}_2-\text{C}_6\text{H}_5$, and that further information could be obtained concerning the correctness of the mechanism postulated for the synthesis and rearrangement of alkamines.

II. DISCUSSION OF THE RESULTS

A. The formation and rearrangement of α, β, β -triphenyl- β -hydroxyethylamine, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})-\text{CH}(\text{NH}_2)-\text{C}_6\text{H}_5$.

When desoxybenzoin oxime was added to a concentrated Grignard reagent² made from bromobenzene, a vigorous reaction took place; α, β, β -triphenyl- β -hydroxyethylamine hydrochloride (m. p. 236-7°) was obtained upon hydrolysis of the product. The free alkamine³ (m. p. 154°) was liberated from its hydrochloride and shown to be identical with the product obtained by the methods of

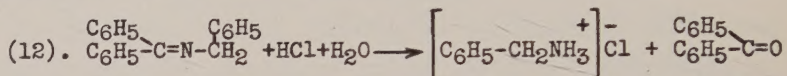
¹Equation (11) combines equations (5) and (6).

²Cole, loc. cit.

³ α, β, β -triphenyl- β -hydroxyethylamine is said to have been prepared by Monte, Gazz. chim. ital., 45, I, 358-62 (1915). The incorrect melting point of 134-36° is given. Paterno, Gazz. chim. ital., 44, I, 247 (1914), is reported to have prepared it from benzophenone and benzylamine and gave the melting point 148-50°.

Thomas¹ and McKenzie.²

This alkamine was rearranged by the method of Lenth,³ i. e., the alkamine was mixed with calcium oxide and heated in an atmosphere of nitrogen for one hour at 250°. A yellowish oil was obtained. It was hydrolyzed by a few drops of dilute acid to benzophenone and benzylamine hydrochloride:



The benzophenone was identified by means of its oxime. The benzylamine was identified by a positive Rimini test,⁴ the formation of a picrate and the analysis of its chloroplatinate. Thus the oil obtained from the rearrangement of α, β, β -triphenyl- β -hydroxyethylamine seemed to be benzophenone benzylimide,

$(\text{C}_6\text{H}_5)_2\text{C}=\text{N}-\text{CH}_2-\text{C}_6\text{H}_5$.⁵ This oil could not be crystallized,⁶ and did not form a stable hydrochloride.⁵

All attempts to isolate either of the intermediate hypo-

¹Thomas and Bettzieche, Zeit. physiol. Chem., **140**, 254 (1924).

²McKenzie and Barrow, J. Chem. Soc., **103**, 1336 (1913).

³Lenth, loc. cit.

⁴Mulliken, Identification of Pure Organic Compounds, (New York: John Wiley and Sons, 1916), II, 35.

⁵Lenth rearranged β, β -diphenyl- β -hydroxyethylamine to methyliminobenzophenone, $(\text{C}_6\text{H}_5)_2\text{C}=\text{N}-\text{CH}_3$, which did not form a stable hydrochloride, and which Mr. Stillson showed did not form a chloroplatinate. Hydrolysis gave benzophenone and methylamine, and reduction with sodium in liquid ammonia gave α -methylamino-diphenylmethane, $(\text{C}_6\text{H}_5)_2\text{CH}-\text{NHCH}_3$.

⁶Benzophenone benzylimide prepared by the method of Redelein, Ber., **53**, 337 (1920), was obtained, after much difficulty, as a white crystalline solid (m. p. 61-2°). Sommelet, Comp. rend., **184**, 1338 (1927), reported that the benzophenone benzylimide obtained by him was definitely an oil. Perhaps the presence of minute impurities in the compound obtained in the above investigation prevented crystallization.

thetical bases, I or II (see pages 2 and 3), from the Grignard mixture during the formation of the alkamine, or from the oil obtained from the rearrangement, were unsuccessful. Consequently, various attempts were made to synthesize them by other methods.

All the alkamine syntheses were run at elevated temperatures, i.e., the Grignard reagent was heated by a hot plate or an oil bath and the dry oxime was added directly to the flask.¹ A study of the temperatures was made during the course of this work. It was concluded that acetophenone oxime reacted at about 125° (which is probably the temperature used by Maver, Cole and others, although it is not stated by them); that desoxybenzoin oxime reacted at about 160°; and that benzophenone oxime reacted at about 170°.²

The yields of the alkamine showed great variation and were never good. During the work on the alkamine many other compounds were isolated from the Grignard reaction (complete experimental details and analyses may be found in the original thesis).³ When

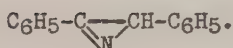
¹It was observed by Maver, Cole and others that a dense white smoke generally accompanied the reaction between the Grignard reagent and the oxime. It was conceded that the best yields were obtained when this smoke was observed. In this work, however, it was found that the presence or absence of the white smoke at 160° seemed to have little effect on the yield of α,β,β -triphenyl- β -hydroxyethylamine. At the low temperatures where the white smoke was never observed, however, no alkamine was formed.

²When dry benzophenone oxime was added to the concentrated Grignard reagent, heated to about 170° on an oil bath, a white solid was obtained (m. p. ca. 145°). It gave on analysis values corresponding to the formula $C_{22}H_{17}N$. Hydrolysis gave aniline and a solid hydrocarbon (m. p. 148°) which has the empirical formula C_4H_3 , and the molecular formula $C_{12}H_8$ or $C_{12}H_{10}$; and a yellowish viscous oil (b. p. 161-2°/11 mm.) which is probably a third compound. The oil has an average molecular weight of about 192, and a refractive index n_D^{20} : 1.6070.

³When it was run at low temperatures stilbene was formed. Occasionally large amounts of diphenylacetophenone (m. p. 136°) were obtained. A white crystalline compound, $(C_{12}H_{11}O)_2$, (m. p. 212°) was sometimes isolated. It has the molecular weight 368. It is probably identical with the compound (m. p. 209-11°) observed by Bettzieche (Zeit. physiol. Chem., 160, 264 (1926)).

the Grignard mixture from the alkamine synthesis was hydrolyzed, the alkamine hydrochloride remained in the aqueous layer, and the oily upper layer was separated by extraction with ether. When the ether was evaporated a red tar remained. When the dried tar was dissolved in anhydrous ether and treated with dry hydrogen chloride gas for a few seconds, a yellowish-white precipitate was formed. This precipitate dissolved upon further passage of the gas. It was very unstable in moist air. The purest samples of this unstable hydrochloride (m. p. about 95°) were obtained when the alkamine Grignard mixture was decomposed with liquid ammonia.¹ Most of the attempts to hydrolyze or study this hydrochloride otherwise resulted in the formation of heavy, dark colored tars. It was observed that when the unstable hydrochloride was suspended in moist alcohol (about 90%) it hydrolyzed slowly to a white compound (m. p. 188-90°), which has a molecular weight of 468.

B. The attempts to form the cyclic ketimine I,



1. The method of Neber and Burgard.²

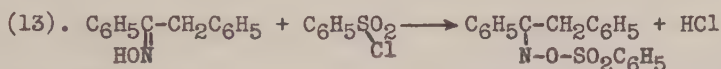
Desoxybenzoin oxime was treated with para-toluenesulphonylchloride in a pyridine solution at 0°. No reaction took place between the oxime and the acid chloride while the mixture stood in the ice-box for thirty-six hours; nor when it was heated on a hot plate for six hours. In each case the oxime was recovered almost quantitatively.

The procedure was then modified, benzenesulphonylchloride being used in place of the para-toluenesulphonylchloride. After

¹Cornell, J. Am. Chem. Soc., 50, 3314 (1928); and J. B. Cloke, Doctorate Dissertation, University of Chicago, 1931, footnote, p. 48.

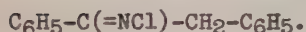
²Neber and Burgard, loc. cit.

the mixture had stood at 0° for thirty-six hours a few white crystals were obtained. These melted at 128° after recrystallization from 95% alcohol. When this compound was hydrolyzed, desoxybenzoin and benzenesulphohydroxamic acid were isolated and identified. The compound of the melting point 128° is probably the benzene-sulphonic acid ester of desoxybenzoin oxime, formed according to the following equation:



The yield of the sulphonic acid ester was not increased by carrying the reaction out at room temperature. In other experiments the mixture was heated on the steam bath for a few hours. This time phenylacetanilide (m. p. 115-6°) was isolated in good yield. The oxime had undergone a Beckmann rearrangement, which is in accordance with the results reported by Werner and Pequet.¹

2. The attempt with N-chlorophenylbenzyl ketimine,



Phenylbenzyl ketimine hydrochloride was prepared by a modification of the method of Moureu and Mignonac.² The structure² of the hydrochloride (m. p. 210-211°) was proved by analysis and by hydrolysis to desoxybenzoin and ammonium chloride. The hydrochloride was converted into the free base, which melted at 57°, and which on analysis gave values corresponding to those for the theoretical formula $\text{C}_{14}\text{H}_{13}\text{N}$.

The melting points of the base and its hydrochloride as

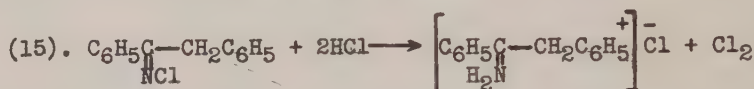
¹Werner and Pequet, Ber., 37, 4307 (1904).

²Moureu and Mignonac, Ann. chim., (9), 14, 322-59 (1920). They did not prove the structure of the hydrochloride conclusively.

found here do not agree with those given by Ectors.¹ The ketimine hydrochloride obtained in the investigation in this laboratory was purified by fractional precipitation from a chloroform solution by ligroin until a constant melting point of 210-211° was obtained. It gave on analysis the following values:

Found, Cl: 15.23%; 15.25%. Calculated, Cl: 15.31%.
N: 5.95%; 5.96%. N: 6.05%.

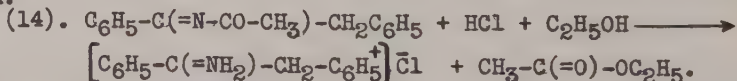
The hydrochloride was converted into N-chlorophenylbenzyl ketimine. This chlorimine was subsequently changed back into the hydrochloride, which then melted at 211°, and did not depress the melting point of the original hydrochloride.



This hydrochloride, obtained from the chlorimine, was hydrolyzed and formed desoxybenzoin and ammonium chloride. The above reactions should preclude any possibility of the hydrochloride (m. p. 210-211°) being contaminated with 3,4,5-triphenylpyrazoline hydrochloride.

The free base, phenylbenzyl ketimine, was liberated from its hydrochloride. It melted at 57°, which is in accordance with

¹Ectors prepared a crude hydrochloride (m. p. about 213°) which he claimed was a mixture of phenylbenzyl ketimine hydrochloride (m. p. 137°) and 3,4,5-triphenylpyrazoline hydrochloride (m. p. 221°). His evidence for this claim was the fact that the free base, liberated from this crude hydrochloride, gave, on distillation under reduced pressure, desoxybenzoin and triphenylpyrazoline. He prepared a compound (m. p. 137°) from N-acetylphenylbenzyl ketimine, which he called phenylbenzyl ketimine hydrochloride, and which he believed was formed according to the following equation:



He liberated a free base from this hydrochloride, which melted at 92-3°. See Ectors, Bull. acad. roy. Belg., Classes des Sciences, (5), 10, 347-52 (1924).

the melting point recorded by Moureu.¹ It was hydrolyzed by moisture to desoxybenzoin and ammonia. It gave on analysis the following values:

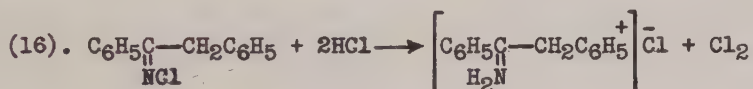
Found, C: 86.01%; 86.09%. Calculated, C: 86.11%.

H: 6.94%; 6.71%. H: 6.72%.

N: 7.00%; 7.07%. N: 7.18%.

Therefore, the hydrochloride (m. p. 137°) and its free base (m. p. 92-3°) which were obtained by Ectors are not phenylbenzyl ketimine and its hydrochloride.

N-bromophenylbenzyl ketimine² was prepared by the method of Young.³ This compound was so unstable that work with it was abandoned. The N-chlorophenylbenzyl ketimine was then made by the method of Peterson.⁴ It was a white solid (m. p. 78°).⁵ Although this chlorimine was not very stable, it was used in the following work. Its structure was proved by the following reaction:



The hydrochloride thus obtained was identical with the original ketimine hydrochloride, and on subsequent hydrolysis

¹Moureu and Mignonac, Comp. rend., **159**, 149-52 (1914).

²N-bromophenylbenzyl ketimine is a cream white solid, melting at about 55°. It is very unstable, decomposing rapidly in air to a sticky yellow gum. The best analysis obtained was: found, "active" Br: 26.72%, calculated for C₁₄H₁₂NBr, "active" Br: 29.17%.

³H. D. Young, Doctorate Dissertation, University of Chicago, 1926. Abstracts of Theses, University of Chicago, Science Series, IV (1925-26), 203-211.

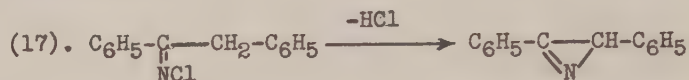
⁴Peterson, Am. Chem. Jour., **46**, 325 (1911).

⁵A chlorimine mixture (m. p. 82°) was obtained when the impure chlorimine fractions were recrystallized from 95% alcohol. It gave on analysis about 12.4% "active" chlorime, and was more stable than the pure chlorimine. See the Experimental Part.

gave desoxybenzoin.

The chlorimine, according to the percentage of "active" chlorine¹ was never obtained more than 90% pure.² It resisted all attempts to purify it further.

Attempts were made to produce the cyclic ketimine I by the following reaction:



This reaction would resemble the formation of nitriles from chlorimino aldehydes as observed by Hauser.³

The chlorimine was heated with silver oxide suspended in dry benzene, and with dry potassium hydroxide in ether, for six hours. Apparently no reaction took place in either case, and the chlorimine was recovered. When the chlorimine was heated with a 3% aqueous solution of potassium hydroxide for a few hours, decomposition took place, and a sticky yellow gum was formed. This gum resisted all attempts to learn its identity. It might have been a polymer, a ketisoketimine,⁴ or a nitrile.⁵ Some benzilic

¹The "active" chlorine is relatively positive, (Cl⁺).

²This degree of purity, calculated from the chlorimine analysis (found, Cl: 13.9%; theoretical, Cl: 15.44%) indicated that N-chloro- α -chlorophenylbenzyl ketimine (theoretical, Cl: 13.33%), $\text{C}_6\text{H}_5\text{C}(=\text{NCl})\text{CH}(\text{Cl})\text{C}_6\text{H}_5$, might have been formed. This, however, is not the case, because the chlorimine was decomposed into desoxybenzoin.

³Hauser et al., J. Am. Chem. Soc., **52**, 4163 (1930).

⁴Moreau and Mignonac, Ann. chim., (9), **14**, 322 (1920). Diphenyl-benzyl-benzylidene ketisoketimine, $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)=\text{N}-\text{C}(\text{C}_6\text{H}_5)=\text{CH}-\text{C}_6\text{H}_5$, is described as a very viscous yellow oil of b. p. 248°-50° at 2 mm. pressure. It hydrolyzes to desoxybenzoin and ammonium chloride. Similar yellow substances were obtained from the decomposition of phenylbenzyl ketimine when it stood in air; from the N-bromo ketimine, which decomposed almost instantly; and from the N-chloro ketimine as noted above.

⁵Raschig, Schwefel und Stickstoff Studien, (Leipzig, Berlin: Verlag Chemie G.m.b.H., 1924), p. 20.

acid (m. p. 150°) was generally obtained when the chlorimine was heated with an aqueous solution of a base. It seemed to be produced in larger quantities when a stronger basic solution was used. Generally the solution went through a series of color changes, yellow to brown to yellow, and developed a carbylamine odor.

C. The attempt to prepare 1,1-diphenyl-2-phenylethylenimine, $(C_6H_5)_2C-CH(-NH)-C_6H_5$.

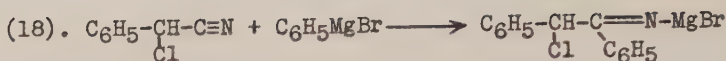
Various attempts were made to produce the cyclic base II $(C_6H_5)_2C-CH(-NH)C_6H_5$, by the action of phenylmagnesium bromide on α -chlorobenzylcyanide, $C_6H_5-CH(Cl)-C\equiv N$. De Booseré¹ was able to prepare 1,1-diethyl-2-propylethylenimine, $(C_2H_5)_2C-CH(-NH)C_3H_7$, by this type of reaction.

From the reaction between phenylmagnesium bromide and α -chlorobenzylcyanide a dark red oil was isolated. This formed a hydrochloride (m. p. about 155°), which was unstable in the presence of moisture. The free base liberated from this hydrochloride had a melting point of about 82°. It was very difficult to purify and formed no satisfactory derivatives. It gave on analysis values corresponding to the formula $C_{28}H_{22}N_2$. The compound was thought to be a polymer of the intermediate cyclic ketimine I. Mathus² stated that during his work on α -chloronitriles he was greatly troubled with polymerization products. Theunis³ had the same difficulty and postulated a mechanism for the formation of one of his dimers. This mechanism applied to α -chlorobenzylcyanide would give 2,3,5,6-tetraphenyl-2,5-dihydro-1,4-diazine.

¹De Booseré, Bull. soc. chim. Belg., **32**, 44 (1923).

²Mathus, Bull. soc. chim. Belg., **34**, 286 (1925).

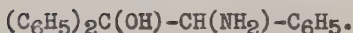
³Theunis, Bull. acad. roy. Belg., Classes des Sciences, **10**, 785 (1926).



It seems quite probable that the dimer obtained in this work was impure 2,3,5,6-tetraphenyl-2,5-dihydro-1,4-diazine, because it possessed many of the general properties which Tutin¹ found in similar 1,4-diazines. The compound $\text{C}_{28}\text{H}_{22}\text{N}_2$ is unsaturated and is oxidized to benzoic acid (m. p. 122°). An attempt was made to determine its structure; but the results obtained were meager, so work was abandoned for the present. 2,3,5,6-Tetraphenyl-2,5-dihydro-1,4-diazine is not recorded in the literature.

III. EXPERIMENTAL PART

A. α,β,β -Triphenyl- β -hydroxyethylamine,



1. Preparation of desoxybenzoin,² $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH}_2-\text{C}_6\text{H}_5.$

Benzoin³ (50 g.) was added to a mixture of pure glacial acetic acid (300 cc.) and water (50cc.). Granulated zinc⁴ (50 g.) was added to the mixture and it was boiled in a 1-liter flask fitted with a reflux condenser⁵ for about twenty-four hours, or until

¹Tutin, J. Chem. Soc., 97, 2495-2524 (1910).

²This is a modification of the method described by Sudborough, J. Chem. Soc., 71, 219 (1897).

³The benzoin was prepared by the method given in Organic Syntheses, (New York: John Wiley and Sons, 1921), I, 33.

⁴The purity of the zinc was very important. The presence of slight impurities caused the yield of desoxybenzoin to diminish greatly. Mallinckrodt's Reagent Zinc, No. 30 mesh, gave the best results.

⁵This operation was carried out in an all-glass apparatus.

most of the zinc was used up. The warm mixture was then poured into ice-water and allowed to stand until the yellow oil solidified. The solid was collected on a filter. It was dissolved in a small amount of ether, and the resulting solution was filtered from the insoluble impurities.¹ After the evaporation of the ether, the crude desoxybenzoin was crystallized from 90% alcohol. Colorless plates were obtained, which melted at 55-6°. The yield was generally about 60% of the theoretical.

2. Preparation of desoxybenzoin oxime, $C_6H_5C(=NOH)CH_2C_6H_5$.

Pure desoxybenzoin (11 g.) and hydroxylamine hydrochloride (12 g.) were dissolved in 75% alcohol (200 cc.). A 50% aqueous solution of potassium hydroxide (40 cc.) was added cautiously and the mixture boiled in a 500 cc. flask fitted with a reflux condenser, for about six hours. The mixture was then poured into cold water (5 volumes) and allowed to stand a few minutes. The water was very slightly acidified with dilute hydrochloric acid, and the precipitated oxime was collected on a filter. It was recrystallized from 95% alcohol. Norite was used to remove any discoloration. The oxime so obtained melted at 98°. The yield was about 90% of the theoretical. The oxime decomposed slowly, and was best preserved in vacuum over phosphorus pentoxide.

3. Preparation of α,β,β -triphenyl- β -hydroxyethylamine hydrochloride,² $\left[(C_6H_5)_2C(OH)-CH(NH_3^+)C_6H_5 \right] Cl^-$

The Grignard reagent was prepared in the usual way from

¹ About 1 g. of β -desoxybenzoin pinacone and less of the α -desoxybenzoin pinacone were formed. These impurities were slightly soluble in cold ether, while desoxybenzoin was very soluble. By the use of ether the pinacones and part of the unused benzoin were removed.

² When large amounts of the alkamine were needed in the latter part of this work, the method of Thomas and Bettzieche was used.

magnesium turnings (6 g.)¹ and bromobenzene (27 cc. diluted with 3 volumes of dry ether). This Grignard reagent was concentrated with the aid of an oil bath.² The excess ether was allowed to distill off by stopping the passage of water through the condenser. The temperature of the oil bath was gradually raised by a hot plate. After sufficient ether had distilled off so that the Grignard reagent would not boil over, the temperature of the bath was maintained at 155-60°. When the Grignard reagent began to become pasty, a thin white smoke developed in the flask. A few minutes later the Grignard reagent changed definitely from a brown paste to a greyish-green mass.² At this point water was allowed to flow through the condenser in order to keep the remaining ether in the Grignard reagent. From this point until the end of the reaction the temperature of the oil bath was kept constant.

Desoxybenzoin oxime³ (10 g.) was then added in small portions to the Grignard reagent through a side arm of the three-neck flask⁴ over a period of five to ten minutes, depending upon the vigor of the reaction. Generally a vigorous reaction took place and the flask was filled with dense white smoke. After all the oxime was added, the mixture was allowed to reflux for about five minutes. The oil bath was then removed and the mixture allowed to cool until it became a thick paste. This paste was poured into a beaker of ice and water. Ammonium chloride was added to the mixture until most of the magnesium hydroxide was dissolved.

¹The ratio of the amount of phenylmagnesium bromide to that of desoxybenzoin oxime was approximately 6 moles to one.

²Cole, loc. cit.

³The oxime should be very pure and dry (dry over P₂O₅ in vacuum for several days).

⁴See the special apparatus described by Cole, loc. cit., p. 16.

The mixture was then made slightly acid with dilute hydrochloric acid. The reddish oily layer¹ was extracted with ether. The aqueous acid solution was set aside. After six to eight hours most of the alkamine hydrochloride precipitated out of the aqueous solution. This precipitate was collected on a filter and crystallized from 95% alcohol. White crystals were obtained which melted at 236°. The yield was 1-2 grams.²

The filtrate from the alkamine hydrochloride was then made basic with ammonium hydroxide. More ammonium chloride was added to keep the magnesium hydroxide in solution. The remainder of the alkamine was thus precipitated as the free base.

4. Preparation of the alkamine, $(C_6H_5)_2C(OH)-CH(NH_2)C_6H_5$.

A dilute aqueous solution of potassium hydroxide was added to an alcoholic solution of the alkamine hydrochloride. This mixture was then diluted with water and the precipitate collected on a filter. The free base is a white crystalline substance, melting at 154°. The alkamine prepared by the above method was found to be identical with that prepared by the methods of Thomas³ and McKenzie.⁴

5. Preparation of the alkamine chloroplatinate.

The alkamine hydrochloride was dissolved in alcohol⁵ and treated with a few drops of a 10% alcoholic⁵ solution of chloro-

¹See p. 7 for products isolated from the oily layer.

²The yields were very poor. The purity of the oxime and the temperature are probably the important factors.

³Thomas, loc. cit.

⁴McKenzie, loc. cit.

⁵All the alcohol used must be free from aldehydes.

platinic acid. The solution was allowed to evaporate in air until crystals of the chloroplatinate began to appear. The chloroplatinate crystallizes in fine orange needles, melting at about 229°, and is much more soluble than the hydrochloride.

Analysis: 0.0380 gm. of substance gave 0.0075 gm. Pt.
Calculated for $(C_{20}H_{20}NO)_2PtCl_6$: Pt, 19.75%; Found: Pt, 19.74%.

6. Rearrangement of α,β,β -triphenyl- β -hydroxyethylamine.

The alkamine (2.0 g.) and dry calcium oxide (1.0 g.) were heated in a large tube fitted with a reflux condenser for one hour at 250° in an atmosphere of dry nitrogen gas.¹ A greenish-yellow oil was formed. When the mixture was cool, this oil was extracted with dry ether. The ether was evaporated and the remaining oil weighed 1.8 grams. All attempts to crystallize this oil or to form a stable hydrochloride were unsuccessful.

A portion of the oil was hydrolyzed with a little warm dilute hydrochloric acid. The mixture was extracted with ether. An oil was obtained on removal of the ether from the above extract. This oil, when treated with hydroxylamine hydrochloride gave an oxime (m. p. 141°) which did not depress the melting point of benzophenone oxime (m. p. 142°).

The aqueous solution from the ether extract was evaporated to dryness on a steam bath. An amine hydrochloride was isolated which gave a positive Rimini test. Portions of the hydrochloride were converted into a picrate (m. p. 197°) which did not depress the melting point of benzylamine picrate (m. p. 197°). A chloroplatinate was prepared, which melted at 220°, the melting point of benzylamine chloroplatinate.

¹Lenth, loc. cit.

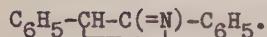
²Benzophenone benzylimide is reported in the literature as both a solid and a liquid. See footnote 6, p. 6.

Analysis by Pregl's micro method:

3.544 mg. of substance gave 1.099 mg. of Pt. Found: Pt, 31.01%; Calculated for $(C_7H_{10}N)_2PtCl_6$: Pt, 31.28%.

Thus the oil obtained from the alkamine seemed to be benzophenone benzylimide, the expected rearrangement product.

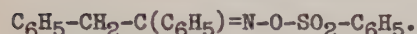
B. The attempts to prepare the cyclic ketimine,



1. The method of Neber.¹

The method of Neber, using para-toluenesulphonylchloride, failed. It was then tried with benzenesulphonylchloride.

(1) Desoxybenzoin oxime benzenesulphonate,



The general procedure was the same as that given by Neber. Desoxybenzoin oxime (10 g.) was dissolved in dry pyridine (16 cc.) and cautiously mixed at 0° with benzenesulphonylchloride (6 cc.) dissolved in dry pyridine (16 cc.). The mixture was allowed to stand in the ice-box for forty-eight hours. Its color gradually darkened to a deep reddish brown. Some crystals were formed. These were collected on a filter and recrystallized from 95% alcohol. About 2 grams of white crystals were thus obtained, which melted at 128°, and were later identified as desoxybenzoin oxime benzenesulphonate. These crystals reduced boiling, aqueous alkaline potassium permanganate solution slowly. Fusion with sodium gave a good test for nitrogen, a very good test for sulphur, and no test for the halogens.

(2) Hydrolysis of the compound (m. p. 128°).

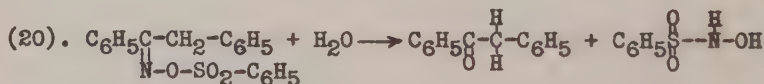
The compound (0.5 g.) was dissolved in a mixture of equal

¹Neber and Burgard, loc. cit.

parts of alcohol and water. A few cubic centimeters of concentrated hydrochloric acid were added, and the resulting mixture heated in a flask fitted with a reflux condenser for about one hour. A white flaky solid separated from the mixture and was collected on a filter. This solid was desoxybenzoin (m. p. 56°). It formed an oxime (m. p. 98°), which did not depress the melting point of known desoxybenzoin oxime (m. p. 98°).

The filtrate from the desoxybenzoin yielded on evaporation some yellowish crystals. These were very soluble in water, 95% alcohol, and slightly soluble in benzene. When recrystallized from benzene they were obtained in the form of long colorless needles which melted at 126°. These crystals reduced boiling Benedict's solution. Fusion with sodium gave a good test for nitrogen and sulphur. These data indicated that the compound was probably benzenesulphohydroxamic acid (m. p. 126°).¹

The compound (m. p. 128°) obtained in part (1) was probably desoxybenzoin oxime benzenesulphonate, and was hydrolyzed according to the following equation:

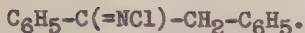


In the hydrolysis, the sulphonic acid group must have moved from oxygen to nitrogen.

¹ Piloty, Ber., 29, 1560 (1896).

A small amount of benzenesulphonic acid was isolated along with the sulphohydroxamic acid. It melted high (66°) and was converted into a barium salt. Angeli, Angelico and Scurti, Atti R. accad. dei Lincei Roma, (5), 11, I, 555, 560; C., 1902, II, 691, reported that benzenesulphohydroxamic acid on hydrolysis with acid yielded benzenesulphonic acid.

2. N-chlorophenylbenzyl ketimine method,



(1) The preparation of phenylbenzyl ketimine hydrochloride,¹ $\left[\text{C}_6\text{H}_5\text{-C(=NH}_2\text{)-CH}_2\text{-C}_6\text{H}_5 \right]^+ \bar{\text{Cl}}$

Benzylmagnesium chloride was prepared from magnesium turnings (19 g.) and benzyl chloride² (110 cc.) in anhydrous ether (480 cc.). After the Grignard reagent was prepared, benzonitrile² (24 cc.) was added to it slowly. A yellowish-white solid precipitated out, and the ether boiled vigorously. When this reaction ceased, the flask was heated, and the mixture allowed to reflux for at least four hours. The Grignard product was then cooled (the flask was packed in ice and salt) and hydrolyzed with ice and ammonium chloride. The mixture was extracted immediately with cold ether. The ether extract was dried over anhydrous sodium sulphate for about one hour at 0°. The ether solution was then saturated with dry hydrogen chloride gas. The crude yellow hydrochloride which precipitated out of the solution was collected on a filter and stored immediately in vacuo, over phosphorus pentoxide. The yield of the crude salt was about 30 grams.

The crude hydrochloride³ was extracted with dry chloroform. The pure hydrochloride was precipitated from the chloroform extract by anhydrous ligroin (b. p. 35-60°). In this way a very light yellow hydrochloride was obtained which melted at 210-211° with decomposition. This hydrochloride was very sensitive

¹This is a modification of the method of Moureu and Mignonac, loc. cit.

²The benzyl chloride and the benzonitrile were previously dried over anhydrous sodium sulphate.

³It was found advisable to extract small portions, and to extract them several times.

to moisture and hydrolyzed with extreme ease.

Analyses:

0.2510 gm. of substance gave 0.1545 gm. AgCl. Found: Cl, 15.23%.

0.2640 gm. of substance gave 0.1628 gm. AgCl. Found: Cl, 15.25%.

Kjeldahl. 0.3979 gm. of substance required 16.94 cc. of 0.1000 N. HCl. Found: N, 5.96%.

0.4963 gm. of substance required 21.10 cc. of 0.1000 N. HCl. Found: N, 5.95%.

Calculated for $C_{14}H_{14}NCl$: Cl, 15.31%; N, 6.05%.

(2). Hydrolysis of phenylbenzyl ketimine hydrochloride.

The ketimine hydrochloride was suspended in warm water. It hydrolyzed instantly to give a white precipitate, melting at 56°. This was identified as desoxybenzoin. When the aqueous filtrate was evaporated to dryness on a steam bath it gave white crystals which proved to be ammonium chloride.

(3). Preparation of phenylbenzyl ketimine (free base),
 $C_6H_5-C(=NH)-CH_2-C_6H_5$.

The pure ketimine hydrochloride was suspended in dry benzene. Dry ammonia gas was passed through the solution until no more was absorbed (about one-half hour). During this operation the flask was kept in a ice bath. The benzene solution was filtered from the precipitated ammonium chloride and the filtrate evaporated under reduced pressure at 0° until the base began to crystallize out. The ketimine base was precipitated by three volumes of dry ligroin (b. p. 35-60°). The ketimine was immediately collected on a filter and sealed in small glass tubes. It is a fine white powder (m. p. 57°) with a nitrile odor. It decomposes rapidly in air to a sticky yellow gum and hydrolyzes

rapidly in moist air to ammonia and desoxybenzoin. The base is slightly soluble in low-boiling ligroin, soluble in ether, and very soluble in benzene.

Analyses:

0.1441 gm. of substance gave 0.0892 gm. of H_2O and 0.4545 gm. of CO_2 . Found: C, 86.02%; H, 6.93%.

0.1850 gm. of substance gave 0.1109 gm. of H_2O and 0.5840 gm. of CO_2 . Found: C, 86.09%; H, 6.71%.

Kjeldahl: 0.2181 gm. of substance required 10.90 cc. of 0.1000 N. HCl. Found: N, 7.00%.

0.1960 gm. of substance required 9.92 cc. of 0.1000 N. HCl. Found: N, 7.07%.

Calculated for $C_{14}H_{13}N$: C, 86.11%; H, 6.72%; N, 7.18%.

(4). Preparation of N-chlorophenylbenzyl ketimine,¹

$C_6H_5-C(=NCl)-CH_2-C_6H_5$.

Sodium hypochlorite solution was prepared by the addition of chlorine (11.5 g.) to a solution of dry sodium carbonate (17 g.) in water (250 cc.), which had been cooled to 4°. Potassium bicarbonate (4 g.) was then added to the solution. After the reaction was completed the ketimine hydrochloride (6 g. in cold chloroform solution) was added, and the flask shaken constantly in an ice bath for ten minutes. The chloroform layer was separated by means of a separatory funnel.² The hypochlorite solution was extracted once with chloroform. The combined extracts were dried over anhydrous sodium sulphate for thirty minutes at 0°. The chloroform was removed by means of suction, until the chlorimine started to crystallize. The chlorimine was then pre-

¹ This was essentially the method of Peterson, loc. cit.

² The stoppers were carefully greased to prevent scratching, as some nitrogen trichloride was formed.

precipitated by the addition of three volumes of dry ligroin (b.p. 40-60°), which was free from unsaturated compounds. The chlorimine is a white solid, melting at 78°. The yield was about three grams. The compound decomposes in air, acquiring a yellow color and the odor of hypochlorous acid. It is slightly soluble in ligroin, and may be crystallized from this solvent.

The chlorimine was never obtained in a state which gave on analysis more than 14% of "active" chlorine. It seemed to decompose very rapidly at first. Gradually the rate of decomposition lessened. It was impractical to try to raise the percentage of chlorine by further purification. When various fractions of the chlorimine, analyzing from 10% to 13% of chlorine, were recrystallized from 95% alcohol a white crystalline substance (m. p. 82°) was obtained which analyzed about 12.4% chlorine. The properties of this substance were not changed by further recrystallization. The chlorimine of this purity seemed to be quite stable and little affected by moisture. Mixtures with higher percentages of chlorine were affected by moisture.

Analysis: (the best obtained)

0.3415 gm. of substance required 24.38 cc. of 0.1104 N. sodium thiosulphate solution. Found: Cl, 13.97%.

0.3260 gm. of substance required 23.30 cc. of 0.1104 N. sodium thiosulphate solution. Found: Cl, 13.99%.

Calculated for $C_{14}H_{12}NCl$: Cl, 15.44%.

(5) Proof of structure of N-chlorophenylbenzyl ketimine.

Some of the purest chlorimine was dissolved in dry ligroin and dry hydrogen chloride gas passed into the solution. A white precipitate was formed (m. p. 210°) which proved to be the ketimine hydrochloride, and which did not depress the melting point of a known sample. When some of the ketimine hydrochloride, ob-

tained from the chlorimine, was hydrolyzed with water desoxybenzoin (m. p. 56°) was produced.

C. Attempt to prepare 1,1-diphenyl-2-phenylethylenimine,
 $(C_6H_5)_2C-CH(-NH)-C_6H_5$.

1. Preparation of α -chlorobenzylcyanide,¹ $C_6H_5CH(Cl)-C\equiv N$.

Mandelic nitrile² (70 g.) was dissolved in dry ether (175 cc.). Thionyl chloride (160 g.) was added to the mixture, which was heated for about three hours in a 1-liter flask fitted with a reflux condenser. It was then distilled under reduced pressure. α -Chlorobenzylcyanide,³ a greenish yellow liquid with a pungent odor, distilled over at 118-22° under a pressure of 20 mm. The yield was 71 grams.

2. Action of Grignard reagent on the cyanide: Preparation of the hydrochloride of a base $C_{28}H_{22}N_2$.

To the Grignard reagent, prepared from magnesium turnings (12 g.) and bromobenzene (53 cc.) dissolved in dry ether (160 cc.), α -chlorobenzylcyanide (25 g.) was added very slowly. There was a rather vigorous reaction and a red precipitate was formed immediately. The mixture became dark brown after a portion of the cyanide had been added. When all the cyanide was added, the mixture was refluxed for two and one-half hours. It was then hydrolyzed with ice and ammonium chloride and extracted with ether; the dark red ethereal solution was dried over anhydrous sodium sulphate for twelve hours. Dry hydrogen chloride gas was then

¹ This is essentially the method of Ingham, J. Chem. Soc., 130, 695 (1927).

² Mandelic nitrile was prepared by the method given in Organic Syntheses (New York: John Wiley and Sons, 1927), VI, 58.

³ The chlorocyanide was not very stable, and turned reddish on standing. It had to be redistilled frequently.

passed into the ethereal solution. A white flocculent precipitate was formed in a few seconds.¹ It was collected on a filter, and immediately placed in a vacuum desiccator over phosphorus pentoxide. This precipitate was never obtained pure because it was hydrolyzed rapidly in moist air. The highest melting point obtained for a slightly yellow precipitate was 155°. The yield of the impure precipitate was generally about five grams.

3. Preparation of the free base, $C_{28}H_{22}N_2$.

The unstable hydrochloride was suspended in ether and this mixture shaken with cold 2-normal sodium carbonate solution. The ether was removed by evaporation, and the resulting red gum dried in a vacuum desiccator. All attempts to purify this compound by crystallization from various solvents, mixtures of solvents, or by precipitation from various solvents, failed. It could not be steam distilled, or distilled in vacuo at a pressure of 1.5 mm. (temperature of oil bath 250°). The base was purified somewhat by being converted again into its hydrochloride from which it was subsequently set free. In this way a reddish gum was obtained which yielded reddish-brown scales (m. p. ca. 82°), when it was dried in vacuo over phosphorus pentoxide.

The base reduced boiling, aqueous, alkaline potassium permanganate solution. It reacted with bromine in carbon tetrachloride to give a precipitate which redissolved when more bromine was added. Boiling the base with a 25% aqueous potassium hydroxide solution failed to decompose it. No derivatives of the base could be obtained with picric acid, picramic acid, picrolonic acid, oxalic acid, or phthalic anhydride. Chloroplatinates were formed, but they were always contaminated with platinum black because of

¹ The precipitate dissolved upon longer passage of HCl.

the reducing action of the base.

Analyses by Pregl's micro method:¹

3.066 mgs. of substance gave 1.537 mgs. H_2O and 9.640 mgs. CO_2 . Found: C, 85.75%; H, 5.61%.

3.131 mgs. of substance gave 1.580 mgs. H_2O and 9.840 mgs. CO_2 . Found: C, 85.72%; H, 5.65%.

2.601 mgs. of substance gave 0.173 cc. (corrected) N_2 at 31° and 744 mm. (corrected). Found: N, 7.31%.

2.902 mgs. of substance gave 0.194 cc. (corrected) N_2 at 30° and 742.6 mm. (corrected). Found: N, 7.36%.

From these data the empirical formula $C_{14}H_{11}N$ was calculated.

Molecular weight determinations by Pregl's micro boiling point method:

18.311 mgs. of substance; 1.318 gms. of benzene.

t_0	t_1	$\Delta t = 0.088^\circ$, $K = 25.7$
1.822°	1.910°	
1.822°	1.910°	Mol. wt. found: 405.6

29.779 mgs. of substance; 1.318 gms. of benzene.

t_0	t_1	$\Delta t = 0.166^\circ$, $K = 25.7$
1.822°	1.988°	
1.822°	1.988°	Mol. wt. found: 349.7

Molecular weight determination by the camphor method:

17.9 mgs. of substance; 267.0 mgs. of camphor.

t_0	t_1	$\Delta t = 8.0^\circ$, $K = 40.0^\circ$
177.0°	169.0°	Mol. wt. found: 335

The free base must, therefore, be a dimer of $C_{14}H_{11}N$.

Calculated for $(C_{14}H_{11}N)_2$: Mol. wt., 386.

¹These analyses are slightly low because the compound was very difficult to burn and left a slight inorganic residue.

4. Reduction and oxidation of the free base, $C_{28}H_{22}N_2$.

(1) Reduction.

Reduction with zinc in 90% glacial acetic acid gave a reddish-purple solid which was white when precipitated by the addition of water. It turned from red to blue when dissolved in ether, and crystallized from ether as a blue solid. When it was dissolved in cold concentrated sulphuric acid, it imparted a yellow-green color to the solution. The reddish-purple compound did not reduce boiling, aqueous alkaline potassium permanganate solution. It melted at 210° .

Molecular weight determinations by Pregl's micro boiling point method:

12.355 mgs. of substance; 1.318 gms. of benzene.

t_0	t_1	$\Delta t = 0.080^\circ, K = 25.7$
1.960°	2.040°	
1.960°	2.040°	Mol. wt. found: 301.0

26.202 mgs. of substance; 1.318 gms. of benzene.

t_0	t_1	$\Delta t = 0.167^\circ, K = 25.7$
1.960°	2.127°	
1.960°	2.127°	Mol. wt. found: 305.8

(2) Oxidation.

The compound was boiled in a flask fitted with a reflux condenser for twenty-four hours with a chromic acid mixture. Only benzoic acid (m. p. 122°) was isolated.

SUMMARY

1. Phenylmagnesium bromide reacted with desoxybenzoin oxime, $C_6H_5C(=NOH)-CH_2-C_6H_5$, to give α, β, β -triphenyl- β -hydroxyethylamine, $(C_6H_5)_2C(OH)-CH(NH_2)-C_6H_5$. A mechanism for its formation was suggested and discussed.

2. α, β, β -Triphenyl- β -hydroxyethylamine was rearranged to benzophenone benzylimide, $(C_6H_5)_2C=N-CH_2-C_6H_5$. (See note, p. 2.)

3. Attempts were made to form the cyclic ketimine, $C_6H_5-CH-C(=N)-C_6H_5$, by the method of Neber. The desoxybenzoin oxime did not react with para-toluenesulphonylchloride at either low or high temperatures. It reacted with benzenesulphonylchloride at low temperatures to yield desoxybenzoin oxime benzenesulphonate, $C_6H_5-CH_2C(C_6H_5)=N-OSO_2-C_6H_5$. At higher temperatures the oxime yielded phenylacetanilide by a Beckmann rearrangement.

4. Attempts were made to form the cyclic ketimine from N-chlorophenylbenzyl ketimine, $C_6H_5-CH_2-C(=NCl)-C_6H_5$. Phenylbenzyl ketimine hydrochloride, its free base, and N-chlorophenylbenzyl ketimine were prepared. All attempts to split hydrogen chloride from the chlorimine and thus obtain the cyclic ketimine were unsuccessful.

5. Attempts were made to form 1,1-diphenyl-2-phenylethyl-enimine, $(C_6H_5)_2C-CH(NH)C_6H_5$, by the action of phenylmagnesium bromide on α -chlorobenzylcyanide, $C_6H_5-CH(Cl)-C\equiv N$. A dimer $C_{28}H_{22}N_2$ was obtained which was partially identified as a 1,4-diazine.

+++++

I wish to express my deep appreciation of the inspiring guidance of Professor Stieglitz. I am also much indebted to Dr. Irving E. Muskat and to Dr. Leslie Hellerman for many helpful suggestions.

